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(54) **Heat-sensitive recording materials.**

(57) A heat-sensitive recording material comprising a support, a heat-sensitive recording layer containing a color former and a color developer forming color by the contact with the color former formed on the support, an interlayer containing a water-soluble resin or a water-dispersible resin as the main component formed on the heat-sensitive recording layer, and an overcoat layer formed by forming a layer containing (1) a macromonomer having a polymerizable functional group at one terminal of the molecular chain, the main component of the segment being organopolysiloxane and (2) a resin ca-

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## EUROPEAN SEARCH REPORT

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EP 89 10 7769

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	US-A-4604635 (C.A.WIKLOF ET AL) * abstract * * column 2, line 55 - column 4, line 36 * ---	1-7	B41M5/26
Y,D	EP-A-264827 (KANZAKI PAPER MANUFACTURING CO LTD) * abstract * * page 6, line 46 - page 9, line 29 * ---	1-7	
A	GB-A-2181563 (FUJI PHOTO FILM CO., LTD.) * abstract * * page 2, line 9 - page 3, line 30 * ---	1	
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 83 (M-290)(1520) 17 April 1984, & JP-A-59 1296 (RICOH K.K.) 06 January 1984, * the whole document * ---	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05 SEPTEMBER 1990	Examiner MARKHAM R.
CATEGORY OF CITED DOCUMENTS			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date X : particularly relevant if taken alone			

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(71) Applicant King-Seeley Thermos Co (USA-Delaware), 2700 Sanders Road, Prospect Heights, Illinois 60070, United States of America	(58) Field of search C3K C3P C3L C3V
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(54) Antistatic resin composition and laminates containing the same

(57) An antistatic resin composition which is the electron radiation cured reaction product of an electron radiation curable prepolymer and an electron radiation reactive antistatic agent soluble in the prepolymer. An antistatic laminate is made by applying a mixture of the prepolymer and antistatic agent to a substrate and then contacting the mixture with electron radiation.

## SPECIFICATION

## Antistatic resin composition and laminates containing the same

5 This invention relates to resin compositions having antistatic characteristics. More particularly, this invention relates to resin compositions comprising an electron radiation cured product of an electron radiation curable resin precursor and an electron radiation reactive antistatic agent. In other aspects, the present invention relates to a method of making an antistatic resin composition and further to substrate sheets coated therewith. Plastics such as polyethylene, polypropylene and the like are poor conductors of electricity and have a tendency to develop and retain electrostatic charges which attract and hold dust particles. This tendency can have a detrimental effect on the appearance of the plastic, but is especially detrimental for plastic films which are used as packaging materials for delicate electronic devices, such as floppy discs for computers, or are used for hospital operating room supplies. For these kinds of uses, electrostatic charges can have a detrimental effect on the function of the plastic material. It is, of course, also well known that the build up of electrostatic charges in plastic films leads to handling and other problems in manufacturing or converting processes, especially where plastic films are transported at high speed.

One method which can be used to reduce the build up of static electricity in plastics is to add a nonreactive antistatic additive, such as a quaternary ammonium compound or carbon, when compounding the plastic matrix. The additive exudes to the surface of the plastic during processing and reduces the build up of static electricity at the surface of the plastic. This method, however, offers only short term antistatic protection. Another method for reducing static build-up involves providing a light vacuum metallized film on the plastic resin. This method, however, suffers from the disadvantage of environmental instability since the metal used to provide the conductivity characteristics is susceptible to attack by moisture and or other corrosive conditions.

Thus, it would be highly desirable to provide a resin composition having a reduced tendency to form static charges both before and after fabrication and to provide antistatic laminations comprising the resin composition. It also would be highly desirable to develop a more permanent method involving copolymerizing or cross-linking an antistatic agent with a resin to provide long lasting antistatic characteristics throughout the resin.

In accordance with the present invention, it has been found that resin compositions having desirable antistatic properties can be provided by electron radiation curing a composition comprising an electron radiation curable resin precursor and an electron radiation reactive antistatic agent. The antistatic composition can be used to coat a substrate sheet to provide an antistatic lamination. Further understanding of the present invention will be had from the following disclosure wherein all parts and percentages are by weight unless otherwise indicated.

*Summary of the invention*

In accordance with the present invention, an antistatic resin composition comprises the electron radiation cured reaction product of:

(A) an electron radiation curable prepolymer; and (B) an effective amount of an electron radiation reactive antistatic agent soluble in said prepolymer. In accordance with the method of the present invention, an antistatic resin composition is made by (A) mixing an electron radiation curable prepolymer and an effective amount of an electron radiation reactive antistatic agent to form a mixture thereof; and (B) contacting said mixture with electron radiation in an amount sufficient to cure said mixture. Further in accordance with the present invention the antistatic resin may be provided as an antistatic coating on a substrate, such as a metallized substrate sheet. Preferably the antistatic agent is a quaternary ammonium salt.

*Description of the invention*

The antistatic resin composition of the present invention broadly comprises the reaction product of a radiation curable precursor and an effective amount of a radiation reactive antistatic agent. In accordance with the method of the present invention, the antistatic resin composition is made by mixing a radiation curable resin precursor and a radiation reactive antistatic agent to provide a mixture thereof. The reactive antistatic agent is employed in an amount which is effective to obtain the desired antistatic properties. The mixture is then contacted with electron radiation in sufficient amount to cure the mixture. During radiation curing, the antistatic agent reacts with the radiation curable resin precursor to form a polymerized resin having long lasting antistatic characteristics.

The antistatic resin compositions of the present invention are especially useful as coating materials and in one embodiment of the present invention, an antistatic coating of the present invention is provided on

the art. Generally speaking, the radiation curable precursor comprises a mixture of at least one oligomer and mono and/or multi-functional monomers. Generally speaking, the oligomers constitute the backbone of a radiation curable coating and largely determine the ultimate performance of the finally cured coating. Many oligomers are based on acrylate chemistry because of ease of synthesis and cost. For example, suitable oligomers include the epoxy-acrylate, polyester-urethane-acrylates, polyether-acrylates, and polyester-acrylates. Acrylated-epoxy resins tend to have good adhesion and chemical resistance properties. Acrylated-urethane-polyesters tend to cure to hard, tough, flexible chemically resistant coatings. Acrylated-polyethers tend to cure to tough, abrasion resistant coatings, and are generally of lower viscosity than polyurethanes and epoxies. Acrylated-polyesters tend to have low viscosity and good weather-ability.

Oligomers, however, when used by themselves may shrink excessively on curing and/or have an unworkable application viscosity. Thus, monomers and other additives, such as flow control agents, will be generally used in combination with oligomers to provide a radiation curable prepolymer. Backbone oligomers can be used in conjunction with a wide variety of monomers, both mono- and multi-functional. It will be appreciated by those skilled in the art that proper selection of monomers contributes to the final cured coating properties by controlling the cross-link density, hardness, flexibility, cure speed, etc., and, hence, the particular monomers selected will depend upon the final coating properties desired. Generally, combinations of mono- and multi-functional monomers will be preferred to achieve the desired results.

Examples of useful mono-functional monomers include:

n-vinyl-2-pyrrolidone, 2-phenoxyethylacrylate, isobutoxymethyl-acrylamide, isobornylacrylate, 2-ethoxyethoxyethylacrylate, and tetrahydrofurfurylacrylate. N-vinyl-2-pyrrolidone is especially useful because of its abrupt viscosity reduction in small amounts, and high response to electron beam radiation.

Suitable multi-functional monomers include: 1, 6-hexanediol diacrylate, tripropyleneglycoldiacrylate, trimethylolpropanetri-acrylate, pentaerythritoltriacylate, and tetraethyleneglycol-diacrylate.

Antistatic agents suitable for use herein are antistatic agents which are electron radiation reactive with the radiation curable resin precursor and which are soluble in the resin precursor. It has been found that useful agents for use herein are quaternary ammonium salts such as trialkylalkyletherammonium salts. A preferred salt is a trialkylalkyletherammonium salt wherein each of the trialkyl groups has from 1 to about 3 carbon atoms, the alkylether group has an alkyl group having from about 4 to about 18 carbon atoms, and the ether group is selected from the group consisting of ethylene oxide and propylene oxide. An example of a preferred salt is triethylalkyletherammonium sulfate, commercially available as Emerstat 6660 from Emery Industries. The antistatic agent is mixed with the radiation curable resin precursor in an amount effective to obtain the desired antistatic characteristics for the resin composition upon curing thereof. The exact amount will vary from resin to resin, antistatic agent to antistatic agent, and intended use for the resulting product.

One advantage of the antistatic resin compositions of the present invention is that they are especially suitable for use as coatings upon substrates. Substrates contemplated for use in combination with the compositions of the present invention include webs, sheets or films such as paper, glass, polymer coated paper, woven and non-woven sheets of various materials, various polymeric films such as polyethylene film, polypropylene film, polyethyleneterephthalate film, polyvinyl chloride film, ionomer resin film and the like, and include metallized substrates.

Coating of the antistatic compositions of the present invention onto a substrate can be done in any conventional manner. Generally speaking, the coating composition will be applied to the substrate surface in the form of a prepolymer and antistatic agent mixture and then cured in situ by means of electron beam radiation. Generally speaking the coating need be applied and cured on only one side of the substrate. Both sides of the substrate generally benefits in obtaining antistatic characteristics even though the substrate has been coated with the antistatic composition only on one side so long as the substrate is not too thick and a sufficient dosage of radiation is employed to cure the coating. This phenomenon can be observed on substrates of thicknesses at least as great as 10 mils and can be observed not only on polymeric films such as polyethylene film, polypropylene film, polyethyleneterephthalate film, polyvinyl chloride film, ionomer resin film and the like, but also on paper, glass and other webs such as can be made from various woven and non-woven fibrous materials. Furthermore, these substrates can have a continuous thin layer of conductive metal such as aluminum deposited thereon as by a conventional vacuum metallizing process and the coating can be applied to the metallized or non-metallized side of the substrate.

The coating can be applied by dip coating, air-knife coating, roll coating, gravure coating, reverse gravure coating, extrusion coating, bead coating, curtain coating, use of wire wound coating rods, and so forth. The coating deposited on the substrate is effective even as a thin coating having a thickness on the order of from 0.1 to 0.5 mils (0.0025 to 0.013 mm). Of course, the viscosity of the coating composition can vary widely depending upon the method of coating which is chosen and the desired end results.

November 7, 1972 to Quintal; No. 3,769,600, October 30, 1973 to Denholm et al; and No. 3,780,308, December 18, 1973 to Nablo. High energy ionizing radiation such as electron beam radiation should be used in sufficient intensity to penetrate substantially all the way through the coating composition to cure the same. Typically dosages in the range of from about 1 to about 6 megarads are employed. Upon contact-  
5 ing the antistatic resin composition with radiation and sufficient intensity to cure the same, the composition used in the present invention is substantially completely converted to a solid product. 5

In a preferred embodiment of the present invention, a continuous thin layer of conductive metal is sandwiched between a substrate and the antistatic coating of the present invention. Thus, a metal layer can be first applied onto a surface of a substrate and then a continuous coating of the antistatic composition is applied to overcoat the metal layer to provide a laminate having especially good antistatic properties. Generally speaking, the antistatic coating will be applied to the metal in the form of an uncured mixture of prepolymer and antistatic agent and then cured *in situ* on the metallic layer. Suitable metals include aluminum, copper, gold, silver, and the like. The metal layer is preferably deposited in a conventional vacuum metallizing step. A resin coated paper with metallized layer thereon especially suitable  
10 to be overcoated with an antistatic resin composition of this invention is taught in U.S. Patent 4,177,310 December 4, 1979 to Steeves, the disclosure of which is specifically incorporated by reference herein. 10

The antistatic resin compositions of the present invention are useful in several types of products. For example, the coating may be used as an overcoating for photographic film or as a packaging film for electronic devices, floppy discs for computers, hospital operating room supplies, and the like.  
15 The present invention is further illustrated by the following examples: 15

#### Example 1

The following ingredients were mixed with stirring:

25	Ingredient	Parts by Weight	25
	radiation curable urethane acrylate oligomer based coating (S-9384 from Raffi and Swanson)	95 parts	30
30	triethylalkyletherammonium sulfate (Emerstat 6660 from Emery Industries)	5 parts	35

After the triethylalkyletherammonium sulfate was completely dissolved, an about 0.3 mil (0.0076mm) thick coating of the mixture was applied on the aluminum vacuum metallized side of a sheet of 5 mil (0.13mm) thick polyethylene terephthalate film by a no. 4 wire wound rod. The coating was cured by a 2  
40 megarad dose of electron beam radiation. 40

#### Example II

The following ingredients were mixed with stirring:

45	Ingredient	Parts by Weight	45
	radiation curable urethane acrylate oligomer based coating (S-9384 from Raffi and Swanson)	90 parts	50
50	triethylalkyletherammonium sulfate (Emerstat 6660 from Emery Industries)	10 parts	55

After the triethylalkyletherammonium sulfate was completely dissolved, an about 0.3 mil (0.0076mm) thick coating was applied on the aluminum vacuum metallized side of a sheet of 5 mil (0.13mm) thick polyethylene terephthalate and cured as in Example I. 55

*Example III*

The following ingredients were mixed with stirring:

	<i>Ingredient</i>	<i>Parts by Weight</i>	
5	radiation curable urethane acrylate oligomer based coating (S-9384 from Raffi and Swanson)	85 parts	5
10	triethylalkyletherammonium sulfate (Emerstat 6660 from Emery Industries)	15 parts	10

15 After the triethylalkyletherammonium sulfate was completely dissolved, an about 0.3 mil (0.0076mm) thick coating was applied on the aluminum vacuum metallized side of a sheet of 5 mil (0.13mm) thick polyethylene terephthalate and cured as in Example I. 15

*Example IV*

20 A Resisitivity half-life test was used to evaluate the products of Examples I-III. Each product was suspended between two poles of an electrode. A 100 volt charge was placed on one of the poles and the time for half of the voltage to discharge was measured. The following results were obtained: 20

	<i>Product of</i>	<i>Time to Half Discharge</i>	
25	Example I	0.4	25
	Example II	0.1	
	Example III	0.3	

30 *Example V* 30

A radiation curable coating vehicle was prepared from tripropylene glycol diacrylate, 70 parts; a diacrylate ester prepared from the diglycidyl ether of bis-phenol A and acrylic acid (Celrad 3600, Celanese Resins Co.) 15 parts; an acrylate urethane based on an aromatic isocyanate, (CMD 6700, Celanese Resins Co.) 14.7 parts; and a silicone type surface active agent (DC-193, Dow-Corning Corp) 0.3 part. 35

To 85 parts of the above vehicle there was added 15 parts of the triethylalkyletherammonium sulfate of Example I. the resultant clear liquid coating having a viscosity of 120 cps was applied by an offset gravure coating station just prior to an electron beam radiation curing unit. The coating was cured with electron beam radiation on the following substrates at the coating weights shown. 40

	<i>Substrate</i>	<i>Coat Wt.</i> <i>(lbs./3000 ft<sup>2</sup>)</i>	<i>(g/m<sup>2</sup>)</i>	
45	1 1/4 mil (0.03mm) low density polyethylene 60 lb. C2S Paper	1.6	(2.6)	45
	1/2 mil (0.013mm) metallized polyethylene terephthalate	5	(8.1)	
	1/2 mil (0.013mm) metallized polyethylene terephthalate	1.3 (Coating on film side)	(2.1)	
	1/2 mil (0.013mm) metallized polyethylene terephthalate	1.3 (Coating on metal side)	(2.1)	
50	1 1/4 mil (0.03mm) metallized low density polyethylene	1.6 (Coating on metal side)	(2.6)	50

Resistance measurements made with a megohm meter (General Radio) showed that all coated surfaces had antistatic properties with readings in the range of 10<sup>9</sup> to 10<sup>10</sup> ohms/sq.

55 A coupling effect was noted when the antistatic coating was applied over metallized surfaces. Readings on an ohm meter were 10-34 ohms/sq. on the coatings on the metal on the metallized 1/2 mil (0.013mm) polyethylene terephthalate, and 150-200 ohms/sq. on the coating on the metal on metallized low density polyethylene. 55

*Example VI*

An antistatic electron beam curable coating was prepared by mixing with stirring the following ingredients:

5	Ingredient	Parts by Weight	5
	tripropylene-glycol diacrylate	58.6	
	epoxy acrylate oligomer (Celrad 3600)	12.4	
10	urethane acrylate oligomer (CMD-6700, Celanese Specialty Resins)	12.2	10
	gamma-Methacryloxypropyl- trimethoxysilane	1.3	
15	silicone surface active agent (DC-193, Dow Corning)	0.5	15
	triethylalkylether ammonium sulfate (Emerstat 6660, Emery Industries)	15.0	

20	The above coating was applied by an offset gravure coating station to a substrate of 1 1/4 mil (0.03mm) low density polyethylene film at a coating weight of 1.6 lbs./3000 ft <sup>2</sup> (2.6 g/m <sup>2</sup> ), and cured at a speed of 200ft/min. (61m/min.) by electron beam radiation at a dose rate of 3 megarads.	20
25	The surface resistivity of the coated side of the above coated polyethylene film was measured at 8.75 × 10 <sup>8</sup> ohm/sq. at 100 volts and 6.7 × 10 <sup>8</sup> ohms/sq. at 300 volts. The surface resistivity of the uncoated side of the film measured 1.2 × 10 <sup>9</sup> ohms/sq. at 100 volts and 1.0 × 10 <sup>9</sup> ohms/sq. at 300 volts.	25

*Example VII*

30	The antistatic electron beam curable coating of Example VI was applied by an offset gravure coating station to the metallized side of 0.5 mil (0.013mm) polyester film (polyethylene terephthalate which had been vacuum metallized with aluminum) at a coating weight of 1.3 lbs/3000 ft. <sup>2</sup> (2.1g/m <sup>2</sup> ), and cured at a speed of 100 ft./min. (30.5m/min) with electron beam radiation at a dose rate of 3 megarads.	30
35	The surface resistivity of the coated side was measured at 2.2 × 10 <sup>8</sup> ohms/sq. at 100 volts and overloaded (too conductive) at 300 volts. The surface resistivity of the uncoated side measured 1.8 × 10 <sup>12</sup> ohms/sq. at 100 volts and 1.6 × 10 <sup>12</sup> ohms/sq. at 300 volts.	35

*Example VIII*

40	Example VI was repeated except that the substrate was 60lb. (per 3300 sq. ft; or 88.8g/m <sup>2</sup> clay coated both sides paper. The surface resistivity of the coated side was 1.1 × 10 <sup>10</sup> ohms/sq. at 100 volts and 1.2 × 10 <sup>10</sup> at 300-volts. The surface resistivity of the uncoated side measured 3.8 × 10 <sup>10</sup> ohms/sq. at 100 volts and 3.5 × 10 <sup>10</sup> ohms/sq. at 300 volts.	40
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*Example IX*

45	Example VI was repeated except that the polyethylene substrate was first metallized by vacuum deposition of aluminum and the coating was applied over the metal. The surface resistivity of the coated side was measured at 1.5 × 10 <sup>8</sup> ohms/sq. at 100 volts and overloaded (too conductive) at 300 volts. The surface resistivity of the uncoated side measured 1.9 × 10 <sup>12</sup> ohms/sq. at 100 volts and 6.2 × 10 <sup>11</sup> ohms/sq. at 300 volts.	45
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50	<i>Example X</i>	50
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Example VI was repeated except that the substrate was 3 mil (0.076 mm) lay flat low density polyethylene tubing. The outside of the tubing was coated at a weight of approximately 1 lb./3000 ft<sup>2</sup> (1.6g/m<sup>2</sup>). The inside of the tubing was found to have an antistatic surface.

55	CLAIMS	55
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	1. An antistatic resin composition comprising the electron radiation cured reaction product of: (A) an electron beam curable prepolymer; and (B) an effective amount of an antistatic agent soluble in said polymer.	
60	2. The antistatic resin composition of claim 1 wherein said antistatic agent is a quaternary ammonium	60



and said ether group is ethylene oxide or propylene oxide.

5. The antistatic resin composition of claim 4 wherein said quaternary ammonium compound is triethylalkyletherammonium sulfate.

6. The antistatic resin composition of any one of claims 1 to 5 wherein the said prepolymer comprises an acrylated epoxy oligomer.

7. The antistatic resin composition of any one of claims 1 to 5 wherein the said prepolymer comprises an acrylated urethane oligomer.

8. An antistatic resin composition as claimed in claim 1 substantially as described in any one of Examples I to III, V or VI.

9. An antistatic laminate comprising:

(A) a substrate; and

(B) as a continuous coating on said substrate, an antistatic resin composition as claimed in any one of claims 1 to 8.

10. The antistatic laminate of claim 9 wherein said substrate is a film comprising polyethylene.

11. The antistatic laminate of claim 9 wherein said substrate is a film comprising polypropylene.

12. The antistatic laminate of claim 9 wherein said substrate is a film comprising polyethylene terephthalate.

13. The antistatic laminate of claim 9 wherein said substrate comprises paper.

14. The antistatic laminate of claim 9 wherein said substrate is a metallized substrate.

15. The antistatic laminate of claim 9 wherein said substrate is a metallized resin coated paper.

16. An antistatic laminate as claimed in claim 9 substantially as described in any one of Examples I to III, and V to X.

17. The method of making an antistatic resin composition as claimed in any one of claims 1 to 8 comprising the steps of:

(A) mixing the electron radiation curable prepolymer and an effective amount of an electron radiation reactive antistatic agent soluble in said prepolymer to form a solution thereof; and

(B) contacting said solution with electron radiation sufficient to cure said solution.

18. The method of making an antistatic laminate as claimed in any one of claims 9 to 16 comprising the steps of:

(A) mixing the electron radiation curable prepolymer and an effective amount of an electron radiation reactive antistatic agent soluble in said prepolymer to form a solution thereof;

(B) applying said solution as a continuous coating onto the substrate; and

(C) contacting said solution with electron radiation sufficient to cure said solution.

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(54) Heat-sensitive recording materials.

(57) A heat-sensitive recording material comprising a support, a heat-sensitive recording layer containing a color former and a color developer forming color by the contact with the color former formed on the support, an interlayer containing a water-soluble resin or a water-dispersible resin as the main component formed on the heat-sensitive recording layer, and an overcoat layer formed by forming a layer containing (1) a macromonomer having a polymerizable functional group at one terminal of the molecular chain, the main component of the segment being organopolysiloxane and (2) a resin capable of being cured by electron beams on the interlayer and curing the layer by the irradiation of electron beams.

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## HEAT-SENSITIVE RECORDING MATERIALS

### FIELD OF THE INVENTION

This invention relates to a heat-sensitive recording material, and more particularly to a heat-sensitive recording material excellent in a paper feed (sticking) property even under a high humidity environment.

### BACKGROUND OF THE INVENTION

10

Hitherto, a heat-sensitive recording material of obtaining colored images by contacting a color former and a color developer by the action of heat by utilizing the reaction of both components. Since such a heat-sensitive recording material is relatively inexpensive and also the recording device is compact and requires fairly easy maintenance, the recording material is used not only as recording media for facsimile and various kinds of computers but also for other wide field of arts such as heat-sensitive labels, etc.

However, a heat-sensitive recording material has weak points in fingerprint resistance and solvent resistance. For example, when the recording layer thereof is brought into contact with a sebum of finger or a solvent, the recording density is reduced or an unnecessary color called as background fog forms.

For solving such a problem, there are proposed a method of coating an aqueous emulsion of a resin having a film-forming faculty and a chemical resistance on the heat-sensitive recording layer as disclosed in JP-A-54-128347 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), a method of coating a solution of a water-soluble polymer such as polyvinyl alcohol, etc., on the heat-sensitive recording layer as disclosed in JP-A-U-56-125354 (the term "JP-A-U" as used herein means an "unexamined published Japanese utility model application"), etc. However, the improvement by these methods is accompanied by new disadvantages and satisfactory results are not always obtained at present.

For example, when a coating of the aqueous resin is applied on the heat-sensitive recording layer, it is required to restrict the drying temperature for preventing coloring of the recording layer with a high temperature drying, whereby curing of the resin layer is, as a matter of course, insufficient to cause a phenomenon of sticking the resin layer to a recording head during the recording.

Accordingly, it has been proposed to coat a resin component capable of being cured by electron beams on the heat-sensitive recording layer and cure the resin component by electron beams. However, such a method is yet insufficient in the preservability of recorded images. In addition, there may also be problems that the electron beam-curable resin layer causes coloration of the heat-sensitive recording layer just after it has been coated or causes fading of recorded images.

As the result of various investigations for solving these problems, the inventors previously discovered that by forming an interlayer of an aqueous resin on the heat-sensitive recording layer and thereafter forming thereon an overcoat layer containing a resin that is curable upon exposure to electron beams, a heat-sensitive recording material showing improved preservability of recorded images without being accompanied by the formation of fog on the recording layer, having widely varying surface characteristics, and having excellent recording characteristics was obtained as shown in JP-A-62-279980.

On the other hand, recently, various printers such as video printers, etc., which can provide high quality images comparable to photographs are used and even with regard to a heat-sensitive recording material for print out, more excellent recording density and gradation have been required. For the purpose, the development of heat-sensitive recording materials using a plastic film or a synthetic paper as the support and having excellent gradation of recorded images has been made and for improving the preservability of recorded images on such a heat-sensitive recording material, it has been attempted to form an overcoat layer of an aqueous resin, etc., on the recording layer. However, when the heat-sensitive recording material having the overcoat layer composed of an aqueous resin is used for recording by a video printer under a high humidity condition, it has been found that the overcoat layer tends to stick to a recording head or paper feed guides to cause paper clogging. Also, the record density is still insufficient.

As the result of various investigations on such problems, the inventors further discovered that by

material giving high recording density, having excellent gradation and preservability of recorded images, and causing no sticking onto a recording head even under a high humidity condition was obtained and previously filed as European Patent 264,827A.

However, it has been clarified that when even the recording material having excellent characteristics as described above is used for recording by a video printer of printing at a particularly high speed, a sticking phenomenon to a recording head still occurs even by using the electron beam-curable resin as the resin for forming the overcoat layer to cause a problem in the paper feed property or sticking (a heat-sensitive recording material sticks to a thermal head and is not fed smoothly). Such a problem can be improved to some extent by the addition of a pigment to the overcoat layer but the aforesaid improvement is still insufficient in paper feed property in a particularly high-humidity condition or a condition of attaching moisture or a sebum of human skin onto the surface of the recording material.

### SUMMARY OF THE INVENTION

The object of this invention is, therefore, to solve the aforesaid problem and to provide a heat-sensitive recording material excellent in paper feed property.

That is, according to this invention, there is provided a heat-sensitive recording material comprising a support, a heat-sensitive recording layer containing a color former and a color developer forming color by the contact with the color former formed on the support, an interlayer composed of a water-soluble resin or a water-dispersible resin as the main component formed on the heat-sensitive recording layer, and a layer containing

(1) a macromonomer having a polymerizable functional group at one terminal of the molecular chain, the main component of the segment being organopolysiloxane, and

(2) a resin curable upon exposure to electron beams formed on the interlayer, said layer being cured by the irradiation of electron beams to form an overcoat layer.

### DETAILED DESCRIPTION OF THE INVENTION

There is not particular restriction on the combination of a color former and a color developer existing in the heat-sensitive recording layer in this invention and any combinations thereof capable of causing coloring reaction by the contact of both components by the action of heat can be used in this invention. For example, there are a combination of a colorless or pale colored basic dye and an inorganic or organic acidic material and a combination of a higher fatty acid metal salt such as ferric stearate and a phenol such as gallic acid.

However, the combination of a basic dye and an acidic material gives very excellent recording characteristics and hence is particularly preferred in this invention.

There are various kinds of colorless or pale colored basic dyes and specific examples thereof are triarylmethane series dyes such as 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p-dimethylaminophenyl)-3-(1,2-dimethylindole-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindole-3-yl)phthalide, 3,3-bis(1,2-dimethylindole-3-yl)-5-dimethylaminophthalide, 3,3-bis(1,2-dimethylindole-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazole-3-yl)-6-dimethylaminophthalide, 3,3-bis(2-phenylindole-3-yl)-6-dimethylaminophthalide, 3-p-dimethylaminophenyl-3-(1-methylpyrrole-3-yl)-6-dimethylaminophthalide, etc.; diphenylmethane series dyes such as 4,4'-bis-dimethylaminobenzhydrylbenzyl ether, N-halophenyl-leucoauramines, N-2,4,5-trichlorophenylleucoauramine, etc.; thiazine series dyes such as benzoyl leucomethylene blue, p-nitrobenzoyl leucomethylene blue, etc.; spiro series dyes such as 3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3-phenyl-spiro-dinaphthopyran, 3-benzyl-spiro-dinaphthopyran, 3-methyl-naphtho(6'-methoxybenzo)spiropyran, 3-propyl-spiro-dibenzopyran, etc.; lactam series dyes such as rhodamine-B-anilinolactam, rhodamine(p-nitroanilino)-lactam, rhodamine(o-chloroanilino)lactam, etc.; and fluoran series dyes such as 3-dimethylamino-7-methoxyfluoran, 3-diethylamino-6-methoxyfluoran, 3-diethylamino-7-methoxyfluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-6,7-dimethylfluoran, 3-(N-ethyl-p-toluidino)-7-methylfluoran, 3-diethylamino-7-N-acetyl-N-methylaminofluoran, 3-diethylamino-7-N-methylaminofluoran, 3-diethylamino-7-dibenzylaminofluoran, 3-diethylamino-7-N-methyl-N-benzylaminofluoran, 3-diethylamino-7-N-



European Patent  
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## EUROPEAN SEARCH REPORT

Application Number

EP 89 10 7769

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	US-A-4604635 (C.A.WIKLOF ET AL) * abstract * * column 2, line 55 - column 4, line 36 *	1-7	B41M5/26
Y,D	EP-A-264827 (KANZAKI PAPER MANUFACTURING CO LTD) * abstract * * page 6, line 46 - page 9, line 29 *	1-7	
A	GB-A-2181563 (FUJI PHOTO FILM CO., LTD.) * abstract * * page 2, line 9 - page 3, line 30 *	1	
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 83 (M-290)(1520) 17 April 1984, & JP-A-59 1296 (RICOH K.K.) 06 January 1984, * the whole document *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05 SEPTEMBER 1990	Examiner MARKHAM R.
CATEGORY OF CITED DOCUMENTS			
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